

BLEACHING OF MEDIUM CONSISTENCY PULP WITH OZONE
WITHOUT HIGH SHEAR MIXING

FIELD OF THE INVENTION

[0001] The present invention relates to a method of bleaching medium consistency pulp with an ozone-containing gas. More particularly, the present invention relates to the proper utilization of the very fast reaction of ozone, by providing efficient but pulp-preserving mixing immediately on introducing a substantial amount of ozone into the pulp.

BACKGROUND OF THE INVENTION

[0002] A number of methods for the bleaching of pulp with ozone are known in the art. These methods have developed with the goal of carrying out the bleaching stage with medium consistency pulp, i.e. having a consistency of about 7 to 16 per cent.

[0003] Generally, ozone bleaching of medium consistency (MC) pulp according to current practice can be described as ozone generation followed by compression before introducing the ozone containing gas into the the MC pulp flow. The gas-liquid-fiber suspension is thus vigorously treated in one or several high shear mixers before the suspension is led into a bleaching tower. The ozone may be introduced at several points along the pulp stream. Vent gases must be treated because of excess ozone which is carried over.

[0004] The principle thus described may well be a result of the application of oxygen bleaching methods. Oxygen, however, operates at a much slower rate, and the temperatures which are used are significantly higher than those employed in ozone bleaching.

[0005] Typical and frequent problems arise from the difficulty in keeping the suspension uniform. Segregation into two-phase flow readily occurs, and the ozonisation rate drops significantly (to 1 or even 0.1 % of its optimum rate). This is a dominant problem, which may be reduced by using a higher quality ozone, resulting in less gas void and consequently less need for vigorous mixing. A typical solution in the

present state of the art is the use of more than one mixer. This does not, however, eliminate the problem, and by applying more shear forces to the pulp, the strength properties of the resulting product are severely affected.

[0006] A basic problem with such mixers is the short residence time, and if mixing time is increased, undesired backmixing may occur.

[0007] After leaving the mixers, the gas-pulp suspension rapidly segregates into two-phase flow having a relatively small gas-liquid interface per unit volume. The chemical consequences of this are low capacity and a non-uniform bleaching result. Obvious evidence of this phenomenon is the significant ozone surplus often remaining after the bleaching stage, representing both a hazard and an economical loss.

[0008] A pulp bleaching method comprising introduction of high pressure ozone in a carrier gas into a pulp stream with vigorous mixing and subsequent removal of carrier gas is disclosed in, e.g. European Patent No. 511,433. The major issue in this patent is the removal of gas from the pulp after injection into the mixer and the reaction is said to take place essentially within ten seconds in a vertical reaction vessel situated immediately following the fluidizing mixer. Gas at about 10 to 13 bar, containing about 3 to 10 % ozone by weight (6.8 vol %) is used. Preferably, the gas-pulp mixture is carried in a horizontal path following the vertical reaction step to effect separation of the large amount of carrier gas involved.

[0009] Austrian patent application no. 2203/92 describes a method wherein medium consistency pulp is treated with an ozone-containing gas comprising more than 120 g O₃ / normal m³ gas (5.6 vol %) whereby the gas is introduced as fine bubbles with a low differential pressure (preferably less than 1 bar). It is considered that using gas with a high ozone content, a sufficient amount of ozone can be suspended into the gas to achieve the desired bleaching. Further, Austrian Patent Application No. 2203/92 discloses the use of mixers with or

without fluidization effects, and of an ozone reaction stage subsequent to the mixing stage, as well as additional ozone addition stages, with degassing stages in between. Characteristically, the highly concentrated ozone is introduced in static mixers at several points, possibly removing the inert carrier gas (normally oxygen) between stages, and the final reaction between ozone and fiber takes place in a bleaching reactor, typically of the traditional upflow type.

[0010] A common feature of several other publications disclosing ozone bleach processes for medium consistency pulp is the use of fluidizing mixers in connection with the injection of ozone-carrying gas, and the use of subsequent, relatively extended reaction stages and gas separation.

[0011] In chemical process terms, MC ozonisation can be described as ozone molecules in a gas phase that must be transported to the vicinity of the fiber and react with the fiber or other substrates. The ozone must diffuse through the gas-liquid interface, through the liquid to the fiber. The applied mixing affects the size and the relative velocity of the gas bubbles, as well as the amount of fiber-liquid interface. The rate limiting step completely dominating the interaction of ozone with the fiber material is the transport of ozone through the gas-liquid interface. The gas-liquid transfer rate in a given volume is heavily dependant on the bubble size, i.e. gas-liquid surface area m^2 gas/ m^3 suspension, and on the partial pressure of ozone. Other rate limiting steps, like diffusion in the fiber material itself, are determined by the nature and the consistency of the pulp, which is primarily affected by the temperature.

[0012] Due to its dependency on mass transfer, the reaction rate of ozone is, theoretically and empirically, first order.

[0013] Consequently, efficient process solutions must be characterized by the following positions

- the residence time distribution (RTD) must follow a plug-flow pattern (in contrast, backmixing commonly occurs in

mixers), which requires special reactor geometry to avoid backmixing e.g appropriate turbine and baffles.

- mean residence time in transfer/mixer/reactor must match transport and reaction times for complete conversion of ozone; consequently reactor diameter, shape and rotation rate of a possible turbine must match flow rate.
- all ozone should be introduced in one step.

[0014] The high gas void, i.e. the low concentration of ozone generated by most present ozone generators, limits the possibilities to improve the situation. Reduced gas void in subsequent generations of ozone generators will reduce the need for mixing and reduce energy requirements, as well as the size of the equipment. Higher ozone concentrations will also increase the ozonisation rate.

SUMMARY OF THE INVENTION

[0015] In accordance with the present invention, these and other objects have now been realized by the invention of a method for bleaching medium consistency cellulose pulp comprising providing a stream of the cellulose pulp, generating a stream of ozone-containing gas having an ozone concentration of at least 20% by weight from pressurized oxygen, and radially injecting the stream of ozone-containing gas into the stream of cellulose pulp so as to provide a stream of bleached cellulose pulp, whereby the cellulose pulp may be bleached without the use of a high sheer mixer. In a preferred embodiment the method includes generating the stream of ozone-containing gas from a mixture of the pressurized oxygen and at least one other gas or liquid.

[0016] In accordance with one embodiment of the method of the present invention, the method includes radially injecting the stream of ozone-containing gas into the stream of cellulose pulp at a pressure of at least 10 bar.

[0017] In accordance with another embodiment of the method of the present invention, the method includes radially injecting the stream of ozone-containing gas into the stream of cellulose pulp from a plurality of nozzles adapted to

direct the ozone-containing gas into the stream of cellulose pulp. Preferably, the method includes radially injecting the stream of ozone-containing gas into the stream of cellulose pulp substantially perpendicularly to the stream of cellulose pulp.

[0018] In accordance with another embodiment of the method of the present invention, the method includes feeding the stream of bleached cellulose pulp to a dynamic low to medium intensity mixer.

[0019] In accordance with another embodiment of the method of the present invention, the method includes radially injecting the stream of ozone-containing gas into the stream of cellulose pulp by means of a plurality of porous metal injectors.

[0020] According to the method of the present invention, high-concentration, high pressure ozone is introduced into the pulp line, in which conditions approaching plug flow are achieved, a high concentration of ozone is reached with a mass transfer area in the suspension which is sufficient for effective delignification.

[0021] According to one embodiment of the method of the present invention, the ozone is introduced using effective injection nozzles providing for the efficient dispersion necessary for obtaining a uniform distribution as well as sufficient mass transfer area to overcome the rate-limiting mass transfer threshold present in methods according to the prior art. Thus, the need for fiber-destroying high shear fluidizing mixers is eliminated.

[0022] According to another embodiment of the method of the present invention, a dynamic low to medium intensity mixer is provided in the pulp stream immediately downstream of the ozone injection site. Such a mixer delivers to the pulp stream amounts of energy which are well below fluidization energies, and do not mechanically affect the fiber.

[0023] With the aid of recent technology, as disclosed, e.g., in Swedish Patent Application No. 9502339-6, ozone with

a concentration of up to 18 to 20 % by volume may be generated. References to concentrations as high as 300 g O₃/Nm³ have been made in prior art publications (e.g. European Application No. 426,652, with a priority date of October 30, 1989), but such concentrations have not been technically feasible until recently. Using a high ozone concentration (300 g per m³ and higher) and at high pressure (10 bars and higher) together with a proper injection technique, the reaction between ozone and fiber can now take place at a rate such that the subsequent use of an upflow bleach tower is not necessary. The gas pressure is obtained by using precompressed oxygen, optionally mixed with other gases or liquids (e.g. argon) to maintain a suitable conductivity for ozone generation.

[0024] Oxygen is the most common carrier gas used for ozone. Highly concentrated ozone is usually considered to be an explosion hazard. As the ozone generating technology has developed, the accepted limit for stable oxygen-ozone mixtures has been repeatedly pushed upwards, and it appears that no absolute concentration limit for the safe handling of ozone has yet been established. Thus, use of very high ozone concentrations may yet be possible, which further facilitates use of methods according to the present invention. According to the present invention, the concentration of ozone in the gas introduced into the pulp stream is sufficient for achieving bleaching without any fiber-destroying mechanical impact.

[0025] The initial distribution of highly concentrated ozone into the pulp is of importance, for the selectivity, as the carbohydrate component itself may be attacked by ozone if exposed for an extended time. The absence of backmixing, as may occur in high shear mixers, and the presence of plug flow conditions counteract this phenomenon.

[Description of preferred embodiments] BRIEF DESCRIPTION OF THE DRAWING

[0026] The present invention will be more fully appreciated

with reference to the following detailed description, which in turn refers to the drawing, in which;

[0027] Figure 1 is a graphical comparison between the changes in reaction rates against time in a prior art ozone pulp bleaching process using a medium consistency mixer, and a process according to the present invention.

DETAILED DESCRIPTION

[0028] The present invention may be appreciated with reference to the following specific examples;

Example 1

[0029] Ozone-carrying gas having a pressure of about 15 bar and an ozone concentration of 14 % by volume is introduced into a medium consistency pulp line carrying 1000 tons/day by means of a collar of radially arranged nozzles. Preferably, the nozzles are arranged to direct the gas radially into the pulp flow, essentially in a direction perpendicular to the pulp flow. A number of nozzles sufficient for evenly distributing the gas must be used. On this production scale, 186 nozzles with an inlet diameter of a maximum of 1 mm may be used.

[0030] A sufficient mean residence time (10 to 40 seconds) must be allowed before any other disturbing action to the pulp.

Example 2

[0031] A medium intensity (low-shear) mixer is adapted into the pulp stream of the previous example, preferably immediately following the gas injection site. The mixer turbine is preferably a double or multiple screw with blade angles and rotation rate balanced to maintain the plug flow residence time distribution (RTD) and giving good radial mixing efficiency. The center blade has a steeper angle than the outer screw blade. Alternatively, porous metal injector devices for introduction of ozone can be arranged peripherically or on the turbine.

[0032] Figure 1 shows a comparison between a system employing a traditional medium consistency mixer with a very

high capacity for a short interval dropping rapidly to zero, compared to a system according to the present invention, with a moderately high capacity kept constant for a long period. The dotted line represents state-of-the-art traditional medium consistency mixer technology. The first, steep section shows the effect of the mixer with high reaction and uniform distribution. The low rate section shows the effect of the corruption of the gas-suspension interface. The reaction takes place with a nonuniform distribution and the pulp is mechanically stressed by high shear mixing.

[0033] The solid line represents a system according to the present invention. Throughout the process, a moderately fast reaction is taking place in a mildly stressed pulp and with a uniform distribution of ozone.

[0034] Table 1 shows a comparison in numbers between a typical conventional MC bleaching system, a state-of-the-art system and a system according to the present invention.

Table 1

| | | Conventional | Modern | Present invention |
|----------------------|------------------------------------|--------------------------------|-------------------------------|---------------------------------|
| | | 1 | | |
| <i>Calculus Base</i> | <i>Units</i> | | | |
| Pulp production | ton OD/day | 1000 | 1000 | 1000 |
| Consistency | % | 10 | 10 | 10 |
| Ozone pressure | bar | 9 | 9 | 15 |
| Ozone concentration | w% | 10 | 14 | 20 |
| | vol% | 7 | 10 | 14 |
| Ozone charge (3-5) | kg/ton OD pulp | 5 | 5 | 5 |
| Ozone generator | kg/h | 208 | 208 | 208 |
| Ozone volume flow | m ³ /s | | | 0,0146 |
| Nozzle diameter | m | | | 0,001 |
| Number of nozzles | | | | 186 |
| <i>Process</i> | | | | |
| Process temperature | °C | 40 | 40 | 40 |
| Process pressure | bar | 7 | 7 | 15 |
| Pulp Flow | ton OD pulp /h | 42 | 42 | 42 |
| Volume Flow | m ³ /h MC pulp | 375 | 375 | 375 |
| Ozone gas charge | m ³ /h at actual press. | 234 | 165 | 53 |
| Gas void * | % | 38 | 31 | 12 |
| <i>Equipment</i> | | Ozone compressor 1-3 mixers | Ozone compressor 1+ mixers | No ozone compressor No mixer |

Bleach
tower

Bleach
tower

Small bleach
reactor

* Note: Gas void is proportional to process problems

[0035] Although the invention herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present invention. It is therefore to be understood that numerous modifications may be made to the illustrative embodiments and that other arrangements may be devised without departing from the spirit and scope of the present invention as defined by the appended claims.